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Ching-cheh Hung
Glenn Research Center, Cleveland, Ohio

Gregory W. Clark
Manchester College, North Manchester, Indiana

Prepared for the
198th Meeting
sponsored by The Electrochemical Society, Inc.
Phoenix, Arizona, October 22–27, 2000

National Aeronautics and
Space Administration

Glenn Research Center

This report contains preliminary
findings, subject to revision as
analysis proceeds.

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EFFECTS OF SURFACE OXYGEN ON THE PERFORMANCE OF CARBON AS AN ANODE IN LITHIUM-ION BATTERIES

Ching-cheh Hung
National Aeronautics and Space Administration
Glenn Research Center
Cleveland, Ohio 44135

Gregory W. Clark
Department of Physics
Manchester College
North Manchester, Indiana 46962

SUMMARY

Carbon materials with similar bulk structure but different surface oxygen were compared for their performance as anodes in lithium-ion battery. The bulk structure was such that the graphene planes were perpendicular to the surface. Three types of surfaces were examined: surface containing C=O type oxygen, surface containing -O-C type oxygen, and surface containing high concentration of active sites. The test involved cycles of lithium insertion into and release from the carbon materials, which was in the half cells of carbon/saturated LiI-50/50 (vol %) EC and DMC/lithium. During the first cycle of lithium insertion, the presence of adsorbed oxygen, -O-C type oxygen, active carbon sites, and C=O type oxygen resulted in the formation of solid-electrolyte interface (SEI) when the carbon's voltage relative to lithium metal was >1.35 , 1 to 1.35, 0.5 to 1, and 0.67 to 0.7 V, respectively. An optimum -O-C type oxygen and a minimum C=O type oxygen was found to increase the reversible and decrease the irreversible capacity of carbon. Active sites on the carbon surface result in a large irreversible capacity and a second lithium insertion-release mechanism. However, this new mechanism has a short cycle life.

INTRODUCTION

In a previous study it was observed that the performance of an experimental carbon anode in a lithium-ion half cell was affected significantly by the method of pretreatment of the anode immediately before the half cell was assembled. The two pretreatment methods used in that study were 540 °C in 1 atm (1.01×10^5 Pa) nitrogen and 180 °C in 5 mm Hg (667 Pa) air. The later method results in an anode that appears to have a longer cycle life and smaller capacity. It was suspected that the differences of these two anodes were resulted from their differences in surface oxygen (ref. 1).

If this hypothesis is true, then the result suggests the possibility that carbon anodes in lithium-ion batteries can be modified by a small amount of oxygen to better meet the needs of their particular applications.

The objective of this research was to confirm this hypothesis. Specifically, well-characterized experimental carbon fibers were pretreated differently to result in samples having similar bulk structure but different surface oxygen. The surface oxygen on these samples was characterized, and the electrochemical properties of these samples in lithium-ion half cells were examined. The possible cause-effect relations between surface oxygen and performance as carbon anodes were then examined, and the possible implication of these results discussed.

EXPERIMENTAL

Carbon

All experimental carbon used in this research was soft carbon obtained by chemical modification of a commercially available graphitized carbon fiber P-100 (BP-Amoco). Physical and structural properties of these

fibers were extensively characterized. Chemical properties of these fibers in the areas of intercalation and fluorination has also been studied extensively (refs. 2 to 7). The knowledge of the precursor as well as the history of the chemical treatments is believed to be as important as the characterization of the experimental carbon in understanding its electrochemical properties.

The graphitized carbon fibers P-100 were chemically modified to result in nongraphitized samples of soft carbon (refs. 6 and 7) for electrochemical test. The chemical modification involved the sequence of

- (1) intercalation: exposing to vaporous bromine and iodine mixture at 110 °C and 1 atm (1.01×10^5 Pa) total pressure for 3 days, where the partial pressures of bromine and iodine were approximately 1 atm and 0, respectively, at the beginning of the reaction, and reached equilibrium with solid I_2 and liquid IBr at the end,
- (2) fluorination: exposing to 3 cycles of pure nitrogen and pure fluorine at 330 to 370 °C and 1 atm (1.01×10^5 Pa), 21 hr each half cycle, to form $CF_{0.65}$,
- (3) defluorination: exposing to 1 atm (1.01×10^5 Pa) $C_4H_4Br_2$ vapor at 370 to 430 °C for 3 hr to remove the majority of the fluorine atoms from fluorocarbon, and
- (4) carbonization: heated to 1000 °C in nitrogen at 1 atm (1.01×10^5 Pa) for 0.5 to 1 hr. This process removes all but traces of noncarbon materials and resulted in many reactive carbon sites.

The presence of bromine and iodine during fluorination is needed in order to result in a complete carbon-fluorine reaction without carbon loss in the form of light fluorocarbon. The presence of $C_4H_4Br_2$ during fluorine removal is important in preventing loss of or damage to carbon structure.

The electrical resistivity and x-ray diffraction data of both the experimental soft carbon thus obtained (after more than 24 hrs of room temperature exposure) and its precursor are summarized in table I. Their atomic force microscopic (AFM) images are shown in figure 1. The soft carbon and its precursor had very different properties and appearance. However, the crystallite distribution and orientation were believed to be similar. In the previous study, it was observed that heat treating both the soft carbon and its precursor to 2700 °C resulted in similar products (ref. 7).

Pretreatment

The purpose of the pretreatment is to let different amounts of oxygen be attached to the carbon surface without making significant changes of the carbon's bulk properties. This was done by letting carbon samples be exposed to air at certain temperature and pressure for a certain period of time immediately after the chemical treatments described above.

The pretreatment of the carbon samples to be electrochemically tested was summarized in figure 2. The pretreatments of their precursor samples were the same as Samples B and C in figure 2, except that the first parts of the processes (intercalation, fluorination, and defluorination) were by-passed.

During room temperature air exposure, all samples were placed in a well-ventilated area. The samples that were exposed to room temperature air for 16 min to 2 days were complete strands of 2000 filaments. For the samples that were exposed to room temperature air for longer than 2 days, every strand of sample was separated into about 10 substrands. The separation of the carbon fibers into small substrands increased the fiber's accessibility to the surrounding air, and was found to significantly increase the rate of oxygen adsorption.

Surface Oxygen Analysis

The samples described in figure 2 were used for electrochemical experiments only. Their surfaces were not characterized. Instead, surfaces of additional carbon samples were examined using x-ray photoelectron spectroscopy (XPS). These samples were treated according to the process described in figure 2, except that the time and the sample's accessibility to the surrounding during room temperature air exposure was slightly different and will be described later in this report. The XPS data obtained from these samples were then used to estimate the oxygen on the surface of the carbon samples that were electrochemically tested.

The XPS analysis focused on amount of surface oxygen and whether it was C-OH and/or C-O-C type or C=O type. The binding energy of the oxygen's 1s electron peaks at 530.6 ± 0.2 eV if the surface oxygen is C=O type, and 532.8 ± 0.4 eV if it is C-OH and/or C-O-C type (ref. 8).

Half Cell Test

The electrochemical properties of the carbon materials were measured in a three-electrode cell containing a counter electrode and a reference electrode of lithium metal, and a working electrode made from a carbon material. Both lithium and carbon fibers were connected to nickel rods, which connected to the electrical instruments. The electrolyte used was saturated LiI in a 50/50 (vol %) mixture of ethylene carbonate and dimethyl carbonate. The half-cell was prepared in a glove bag purged with argon.

During tests, the current was controlled at 10 mA/gm carbon, and the voltage measured. The "cut-off voltage" was set at 0 V for lithium insertion, and 2.5 V for lithium release. In this research, it is assumed that the reversible capacity was approximately equal to the capacity of the last half cycle of lithium release. And, the irreversible capacity was approximately equal to the capacity difference between the first half cycle of lithium insertion and the last half cycle of lithium release.

For the purpose of visually observing the possible interference of lithium salt, a transparent pyrex glass weighing bottle was used as the cell, and LiI was used as the lithium salt. In this arrangement, whenever and wherever I_2 is formed in the cell during reaction, it can be identified by its color. For example, the color of the electrolyte did not change if the lithium release was stopped at 0.7 V, but gradually turned from light yellow to orange after several cycles of cell test if the "cut-off voltage" was 3.0 V.

Trial runs were made using commercially purchased crystalline graphite powder as working electrodes, where nickel screen was used as the substrate, and polyvinylidene fluoride (PVDF) was used as the binder for the graphite powder. The capacity for the first half cycle of lithium insertion to 0 V was measured to be 380 mAh/g of graphite, within experimental error of the literature value (390 to 420 mAh/g).

RESULTS AND DISCUSSIONS

Surface Oxygen

Oxygen content at the surface of the carbon samples examined by XPS is summarized in table II. These samples were treated according to the process described in figure 2, except that the time and the sample's accessibility to the surrounding during room temperature air exposure was slightly different. The differences are also included in table II. Based on the characteristics of their surface oxygen, the samples were divided into 3 groups as follows:

A group (I) of three samples that had similar bulk structure but different chemical states of surface oxygen. This includes sample A, B, and C in figure 2. They were found to have similar resistivity range (900 to $1050 \mu\Omega\text{-cm}$). Also, their (002) x-ray diffraction peaks were at similar location (3.38 Å) and have similar width (0.8°). Their surfaces were found to have low oxygen content, C=O type oxygen (binding energy of the 1s electron 531 eV), and C-OH and/or C-O-C type oxygen (binding energy of the 1s electron 532.5 eV), respectively. It is believed that this difference was a direct result the sample treatment method as described in figure 2.

A group (II) of two precursor samples which was heated in 1000 °C nitrogen, exposed to room temperature air for 16 min, and, respectively, heated in 5 mm Hg air at 180 and 540 °C overnight. Data obtained from these two precursor samples will be used to compare to those obtained from other samples made from them.

A group (III) of six samples that had similar bulk structure and similar surface HO-C and/or C-O-C type oxygen, but different oxygen content. This includes sample C, D, E, F, G and H in figure 2. Again, it is believed that their differences in surface oxygen were a direct result of different room temperature air exposure time, which was unlikely to change their bulk structures significantly.

Formation of Solid-Electrolyte Interface (SEI)

Surface oxygen on carbon could affect the chemistry of SEI formation. The SEI thus formed is critical in determining the performance of the carbon material as the anode in a lithium-ion battery (ref. 9). It is therefore essential to study the effects of surface oxygen on the SEI formation, which occurs during the first half cycle of the electrochemical test.

The first half cycles of two typical samples (Samples C and precursor C) were shown on figure 3. From this figure, dividing voltages were selected at the points where capacity-voltage curves began to change shape. In this study, the entire first half cycles were divided into six periods (>2 V, 1.35 to 2 V, 1 to 1.35 V, 0.7 to 1 V, 0.5 to 0.7 V, and 0 to 0.5 V).

The capacities of every sample during every period was calculated and summarized in table III and will be used to explain the SEI formation in the later sections of this report.

Surface Effects

Figure 4 shows the first cycle of lithium insertion and release of five samples (Groups I and II described above). Again, sample in Group II were precursors of Samples in group I, and the major difference among the three chemically modified samples in Group I was the chemical state of their surface oxygen.

In the subsequent cycles of lithium insertion and release, the capacity of insertion and release were summarized and shown in table IV. The surface oxygen contents of these samples were estimated based on the data in table II and are included in table IV.

From the electrochemical data described in figure 4 and table IV, several phenomena were observed and were described as follows:

Effects of C=O Type Oxygen.—Two samples in figure 4 contain C=O type surface oxygen. One of them was sample B in Group I, the other was the precursor(B). Both of them were treated at 540 °C in 5 mm Hg (667 Pa) air overnight immediately before electrochemical tests or oxygen characterization using XPS. It can be seen in figure 4 that for both of them, immediately after the beginning of their first lithium insertion at 10 mA/g rate, the voltage-capacity curves dropped quickly from 3 to 0.68 V, and slowly rose to form a plateau at 0.7 to 0.75 V range. This suggests the electrochemical reaction of lithium and oxygen (carbonate) at this voltage.

For Sample B, after the voltage-capacity curve passed the plateaus, the voltage bypassed the range of intercalation-deintercalation (between 0 to 0.3V) and quickly reached zero. This result suggests that, if the carbon surface contains C=O type oxygen, its ability to intercalate-deintercalate lithium could be greatly reduced to near zero.

The phenomenon that surface carbonate oxygen causes a reduction of intercalation capacity was not observed for the precursor (P-100). It is not clear why the carbonate oxygen (6.3 percent) at carbon surface could prevent lithium intercalation completely for one sample (Sample B), but not for another (precursor of sample B). One possible explanation is that intercalation into disordered soft carbon is more difficult than intercalation into the more ordered graphitized precursor, and therefore easier to be blocked by the carbonate oxygen surface.

Effects of Reactive Carbon Sites Without Surface Oxygen.—Sample A in figure 2 has low surface oxygen. Also, since it was heated at 540 °C, 1 atm (1.01×10^5 Pa) nitrogen after room temperature exposure, it is believed to have carbon sites that became chemically reactive when oxygen was removed during the heating process. Sample C, on the other hand, had higher surface oxygen (hydroxide) and lower reactive carbon sites because it was treated at lower temperature and pressure in air. Comparing the electrochemical data of these two samples in figure 4 and table IV, it was found that the carbon sample with low surface oxygen and high reactive sites has a larger irreversible capacity. It also had an extra reversible capacity during the half cycles of lithium release when the voltage was larger than 0.3 V.

The extra reversible capacity during the half cycle of lithium release when the voltage was larger than 0.3 V, however, decreased cycle after cycle, as described in figure 5. It can be seen that the parts of capacities that were resulted from intercalation (<0.3 V) remain unchanged during these cycles, but the parts from other mechanism (>0.3 V) decreased. As a result, the total reversible capacity of this sample decreased cycle after cycle, as described in table IV.

To explain the above phenomena, it is suggested that the active carbon sites were the locations where reactions involving lithium ions and carbon occur. During the reactions, some of such sites produced strong lithium-carbon

bonds that did not dissociate during the process of lithium release. Some other sites, however, produced weak lithium-carbon bonds that did dissociate during the process of lithium release. The former resulted in extra irreversible capacity, and the later resulted in extra reversible capacity when the voltage is greater than 0.3 V. In addition, the dissociation of lithium-carbon bonds may result in carbon's structural and SEI damage, and therefore the decreasing reversible capacities after cycles of lithium insertion and release.

Based on the above hypothesis, the first half cycle data for sample A described in figure 2 and table III indicates that the reaction involving lithium and carbon active sites during SEI formation happened at about 0.7 V, where large quantity of lithium ion influx was indicated.

Effects of Surface HO-C and/or C-O-C Type Oxygen.—Again, based on the above hypothesis, it is further suggested that when the active carbon sites were exposed to 1 atm (1.01×10^5 Pa) air at room temperature or 5 mm Hg (667 Pa) air at 180 °C, carbon-oxygen bonds formed at the active sites, where oxygen was of C-OH and/or C-O-C type. In this situation the carbon sites become inert to lithium during the half cycles of lithium insertion, and the large irreversible capacity as well as extra reversible capacity when voltage was above 0.3 V disappeared.

In addition to the above results, the effects of surface HO-C and/or C-O-C type oxygen were further studied from the electrochemical test on the samples in group III, figure 2 (Samples C, D, E, F, G, and H). These were similar samples, except that the concentrations of their surface HO-C and/or C-O-C type oxygen were different. The curves of carbon voltage versus capacity for the first cycles were summarized in figure 6. The capacity data for the first several cycles were summarized in table V. The surface oxygen contents of these samples were estimated based on the data in table II and are included in table V.

Data in table V indicate that there is an optimum oxygen (hydroxide) content where the reversible capacity of the carbon anode reaches maximum. Also, the higher the surface oxygen (hydroxide) content, the lower the cycle numbers needed before the charge and discharge capacities approach to a constant value.

Again, some hypothesis was made to explain the above-described effects by surface oxygen (hydroxide) cannot be found. It appears that the surface oxygen (hydroxide) could contribute positively in the process of SEI formation. The more the surface oxygen (hydroxide), the faster the effective SEI could be formed, and the less the solvent could attack the carbon structure. However, too much oxygen (hydroxide) could result in a SEI layer that is too thick for a complete lithium intercalation.

From table III, it can be seen that the higher the surface oxygen content, the more the contribution to SEI during the 1.35 to 1.0 V period.

Effects of Adsorbed Oxygen.—In table III, it is observed that at the beginning of the first cycle, the voltages of some samples dropped to <1.35 V much quickly than others. The former included soft carbon de-gased at 180 °C, 5 mm Hg air (Group II) and their all samples (precursor and soft carbon) de-gased at 540 °C, 5 mm Hg (667 Pa) air. The later included soft carbon “de-gased” at 540 °C, 1 atm (1.01×10^5 Pa) nitrogen and its precursor de-gased at 180 °C, 5 mm Hg air. There is a general trend that a stronger de-gas condition lead to a shorter period of >1.35 V. Assuming “de-gas” removes adsorbed oxygen, it is believed that the adsorbed oxygen on the carbon surface was a reason for the irreversible capacity in the form of extra SEI formation during the time when the voltage was >1.35 V. Perhaps because the concentration of such oxygen in this study is low, the effects of such SEI formation on the carbon's performance as anode in lithium-ion battery can not be identified from the data presented here.

CONCLUSIONS

The formation and the performance of the SEI, and therefore the performance of the carbon materials as the anode, in lithium-ion battery are affected by different types and concentrations of surface oxygen on carbon.

If the surface oxygen is of C=O type, it causes SEI formation when the carbon voltage was 0.68 V relative to lithium metal. The SEI thus formed had only negative observable effect: It could greatly lower the capacity for the carbon anode to be intercalated with lithium.

If the surface oxygen is of C-OH and/or C-O-C type, the SEI formation at 1 to 1.35 V becomes important. The oxygen content need to be optimal in order to produce an SEI that has optimum thickness: Thick enough to effectively protect the lithium which is subsequently intercalated into carbon, but thin enough to not become a barrier on the path of lithium ion transport.

If the surface oxygen is in the state of loose adsorption, it would cause SEI formation at >1.35 V. The effects of such SEI formation on the carbon's performance as anode cannot be determined in this study because of its low concentration.

On the other hand, if the carbon surface contains low oxygen but high concentration of active sites, it would cause a large amount of SEI formation at about 0.7 V. The SEI thus formed contains some lithium atoms that are tightly bonded, and some lithium atoms that are loosely bonded. The former cannot be removed from SEI during the half cycle of lithium release, and therefore become the source of high irreversible capacity. The later can be removed from SEI during the half cycle of lithium release, and therefore become a new mechanism of reversible capacity. This new mechanism, however, can result in damaged SEI, and therefore short cycle life for the carbon anode.

REFERENCES

1. Hung, C., NASA TM-209437, 1999.
2. Singer, L., *Fuel*, 70, 1981, pp. 839-847.
3. Hoffman, W., *Carbon*, 30 (3), 1992, pp. 315-331.
4. Jaworske, D., Gaier, J., Hung, C., and Banks, B., *SAMPE Quarterly*, 18, 1, 1986, pp. 9-14
5. Hung, C. and Kucera, D., *Carbon*, 32 (8), 1994, pp. 1441-1448
6. Hung, C., U.S. Patent 5,662,683, 1997.
7. Hung, C., NASA TM-106398, 1994.
8. Harvey, J., Kozlowski, C., and Sherwood, P., *Journal of Material Science*, 22, 1987, pp. 1585-1596.
9. Dahn, J., Sleight, A., Shi, H., Way, B., Weydanz, W., Reimers, J., Zhong, Q., and von Saken, U., *Carbon and Graphite as Substitutes for the Lithium Anode in Lithium Batteries*, G. Pistoia (ed.) pp. 1-47, Elsevier, Amsterdam, 1994.

TABLE I.—RESISTIVITY AND X-RAY DIFFRACTION DATA OF GRAPHITIZED CARBON FIBERS P-100 AND A SOFT CARBON MADE FROM P-100 USING THE SEQUENTIAL PROCESSES OF INTERCALATION WITH BROMINE AND IODINE, FLUORINATION IN FLUORINE, DEFLUORINATION IN $\text{BrH}_2\text{C-CH=CH-CH}_2\text{Br}$, AND CARBONATION AT 1000 °C IN N_2 .

| | P-100 | Soft carbon |
|--------------------------------------|-------|-------------|
| Diameter, μm | 10.0 | 12.5 |
| Resistivity, $\mu\Omega\text{-cm}$ | 390 | 1020 |
| X-ray diffraction, 002 | | |
| Peak position, Å | 3.38 | 3.37 |
| Peak width at half max position, deg | 0.45 | 1.0 |
| Relative peak height | 5 | 1 |

TABLE II.—THE TYPE AND THE CONTENT (%) OF THE OXYGEN ON THE SURFACE OF THE CARBON SAMPLES OBTAINED FROM THE PROCESS DESCRIBED IN FIGURE 2, EXCEPT THE SLIGHT DIFFERENCES IN ROOM TEMPERATURE EXPOSURE CONDITIONS AS DESCRIBED IN THE TABLE

| Sample ^a | Room temperature air exposure, 1 st step | | Overnight heating, 2 nd step | | | Oxygen | |
|---------------------|---|------------------------------------|---|--------------------|--------------|---------------|-------------------|
| | Time | Fiber compactness during this step | Temp, °C | Pressure, Pa | Type of gas | Content, at % | Type |
| C | 16 min | single strand | 540 | 1.01×10^5 | N_2 | 1.4 | -O-C ^b |
| C | 16 min | single strand | 540 | 667 | Air | 6.3 | O=C |
| C | 16 min | single strand | 180 | 667 | Air | 4.6 | -O-C |
| C | 22 hr | single strand | 180 | 667 | Air | 5.0 | -O-C |
| C | 32 hr | single strand | 180 | 133 | Air | 4.7 | -O-C |
| C | 30 hr | separated strand | 180 | 667 | Air | 8.2 | -O-C |
| C | 72 hrs | separated strand | 180 | 667 | Air | 8.5 | -O-C |
| C | 150 hr | tight strand | 180 | 667 | Air | 5.1 | -O-C |
| G | 16 min | single strand | 540 | 667 | Air | 6.8 | O=C |
| G | 16 min | single strand | 180 | 667 | Air | 0.9 | -O-C |

^aSample G is graphitized carbon fiber P-100 heated to 1000 °C in N_2 . Sample C is the soft carbon made from P-100 using the sequential processes of intercalation with bromine and iodine, fluorination in fluorine, defluorination in $\text{BrH}_2\text{C-CH=CH-CH}_2\text{Br}$, and carbonation at 1000 °C in N_2 .

^bThis sample has high concentration of active sites and low oxygen concentration.

TABLE III.—THE CAPACITIES OF THE SAMPLES STUDIED IN THIS REPORT DURING DIFFERENT PERIODS IN THE FIRST HALF CYCLE OF THE LITHIUM INSERTION

| Sample ^a | | Surface oxygen | | Capacities during the periods of different voltage ranges in the 1 st half cycle, mAh/gm | | | | | |
|---------------------|--------------------|----------------------------|-------------------|---|-------------|-------------|------------|--------------------|-----------|
| Label | Group ^b | Content, at % ^c | Type | >2 V | 1.35 to 2 V | 1 to 1.35 V | 0.7 to 1 V | 0.5 to 0.7V | 0 to 0.5V |
| A | I | 1.5 | -O-C ^e | 1.4 | 4.6 | 2.9 | 82.6 | 71.8 | 303.1 |
| B | I | 6 | O=C | 0 | 0 | 0.05 | 1.0 | 130.8 ^d | 29.9 |
| C | I & III | 4.5 | -O-C | 0.04 | 0.86 | 2.6 | 55.2 | 22.4 | 255.7 |
| D | III | 4.5 | -O-C | 0.11 | 2.1 | 4.2 | 57.1 | 25.9 | 269.3 |
| E | III | 5 | -O-C | 0.2 | 1.1 | 7.8 | 53 | 21.9 | 285.6 |
| F | III | 5 | -O-C | 0.08 | 1 | 6.9 | 56 | 23.4 | 274.7 |
| G | III | 9 | -O-C | 0.3 | 2.1 | 8.3 | 44.5 | 19.3 | 260.2 |
| H | III | 9 | -O-C | 0.3 | 1.5 | 8.2 | 44.5 | 19.9 | 261.5 |
| Precursor (B) | II | 7 | O=C | 0.4 | 0.8 | 0.9 | 3.7 | 44.2 | 250.3 |
| Precursor (C) | II | 1 | -O-C | 4.1 | 0.5 | 2.5 | 4.9 | 6.7 | 238.3 |

^aSamples A to H were obtained from the process described in figure 2. Precursor (C) and precursor (B) were obtained in the same way as sample C and sample B, respectively, except the first 3 steps (intercalation, fluorination, and defluorination) were by-passed.

^bThe samples were divided into 3 groups to facilitate data comparison.

^cSurface oxygen was estimated based on the result described in table II.

^dIn this particular sample, the voltage quickly dropped to 0.68 V, then increased slowly to a maximum of 0.78 V, and then slowly decrease to 0.5 V. The capacities were 0.7, 33.8 and 96.3 mAh/g during the sub-divisions of 0.7 to 0.68 V, 0.68 to 0.78 V, and 0.78 to 0.5 V, respectively.

^eThis sample has high concentration of active sites and low oxygen concentration.

TABLE IV.—THE CAPACITIES (mAh/g) OF ELECTROCHEMICAL INSERTION AND RELEASE OF LITHIUM IONS AT 10 mA/g RATE FOR SAMPLES A, B, C, PRECURSOR (B) AND PRECURSOR (C) DESCRIBED IN TABLE III

| Sample | (b) | Cycle number | | | | | | | | | Irreversible capacities ^a |
|---------------------|-----|--------------|-----|-----|-----|-----|-----|-----|-----|-----|--------------------------------------|
| Oxygen ^a | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | |
| A | I | 466 | 315 | 309 | 303 | 301 | 296 | | | | 177 |
| 1.5% -O-C | R | 304 | 301 | 295 | 295 | 292 | 289 | | | | |
| B | I | 161 | 95 | | | | | | | | 75 |
| 6% =O | R | 95 | 86 | | | | | | | | |
| C | I | 337 | 251 | 251 | 249 | 247 | 248 | 249 | 248 | 249 | 91 |
| 4.5% -O-C | R | 252 | 249 | 249 | 247 | 246 | 247 | 247 | 247 | 246 | |
| Precursor (C) | I | 257 | 242 | 246 | | | | | | | 13 |
| 1% -O-C | R | 245 | 241 | 244 | | | | | | | |
| Precursor (B) | I | 298 | 274 | 274 | 272 | | | | | | 30 |
| 7% =O | R | 272 | 271 | 271 | 268 | | | | | | |

^aOxygen type and at %.

^bEqual to the difference between the capacity of the first lithium insertion and the capacity of the last lithium release.

TABLE V.—THE CAPACITIES (mAh/g) OF ELECTROCHEMICAL INSERTION AND RELEASE OF LITHIUM IONS AT 10 mA/g RATE FOR SAMPLES D, E, F, G, AND H DESCRIBED IN FIGURE 4 AND TABLE 3.

| Sample | (b) | Cycle number | | | | | | | | | Irreversible capacities ^a |
|--------------------------|-----|--------------|-----|-----|-----|-----|-----|-----|-----|-----|--------------------------------------|
| Oxygen at % ^a | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | |
| C | I | 337 | 251 | 251 | 249 | 247 | 248 | 249 | 248 | 249 | 91 |
| 4.5% | R | 252 | 249 | 249 | 247 | 246 | 247 | 247 | 247 | 246 | |
| D | I | 359 | 260 | 258 | 254 | 254 | 254 | 254 | | | 106 |
| 4.5% | R | 259 | 256 | 254 | 254 | 254 | 254 | 253 | | | |
| E | I | 370 | 283 | 279 | 277 | 276 | 275 | | | | 95 |
| 5% | R | 280 | 276 | 277 | 276 | 275 | 275 | | | | |
| F | I | 362 | 268 | 266 | | | | | | | 99 |
| 5% | R | 267 | 265 | 263 | | | | | | | |
| G | I | 335 | 252 | 250 | 249 | 247 | 247 | 246 | | | 88 |
| 9% | R | 250 | 249 | 249 | 249 | 248 | 248 | 247 | | | |
| H | I | 334 | 252 | | | | | | | | 85 |
| 9% | R | 250 | 249 | | | | | | | | |

^aThe surface oxygen on the samples described in this table had the oxidation state of hydroxide.

^bEqual to the difference between the capacity of the first lithium insertion and the capacity of the last lithium release.

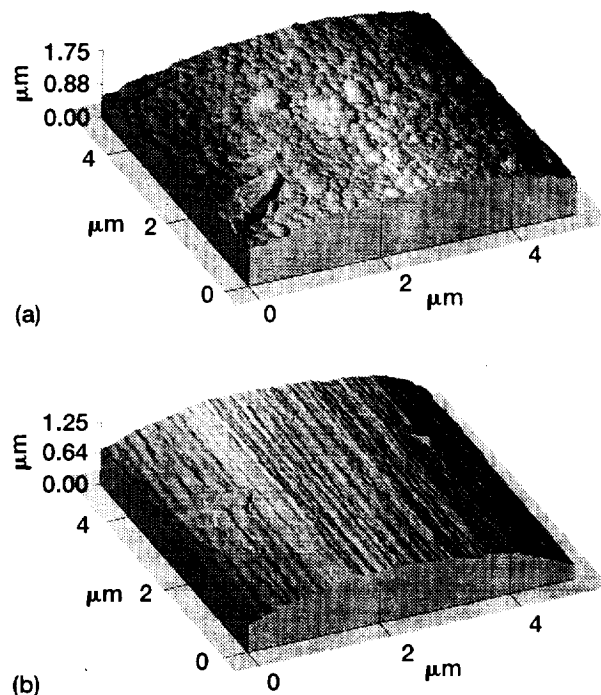


Figure 1(a).—Atomic force microscopy of surfaces of the soft carbon electrochemically tested in this study. (b). Atomic force microscopy of surfaces of the precursor electrochemically tested in this study. Data taken after the samples were exposed to ambient air for more than 1 week.

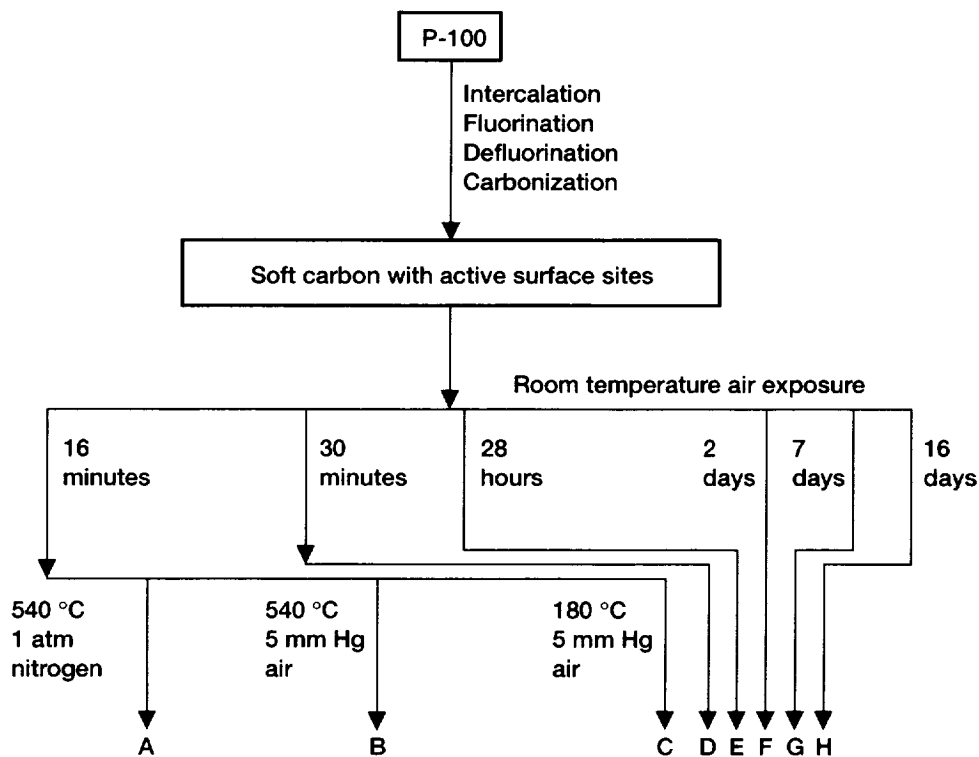


Figure 2.—Pretreatments of the carbon samples electrochemically tested in this research.

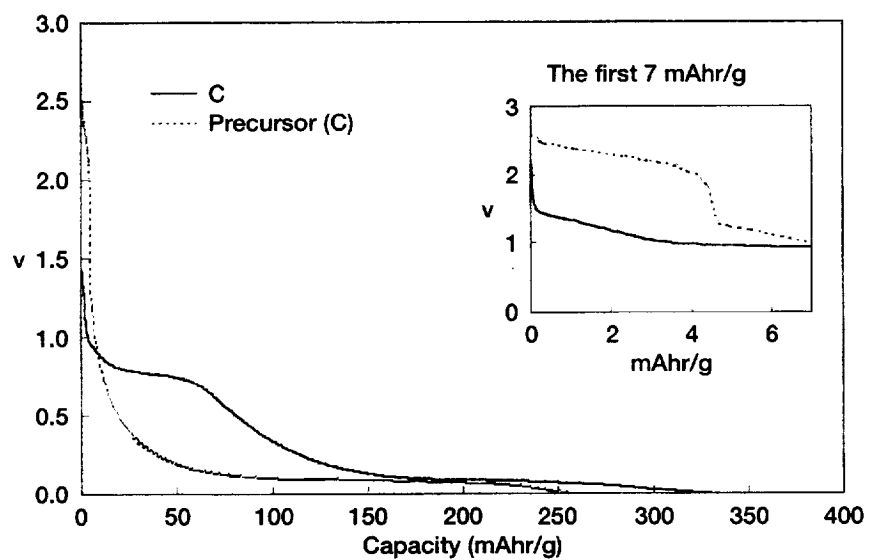


Figure 3.—Carbon electrode voltage during the first half cycle of lithium insertion for sample C and precursor (C).

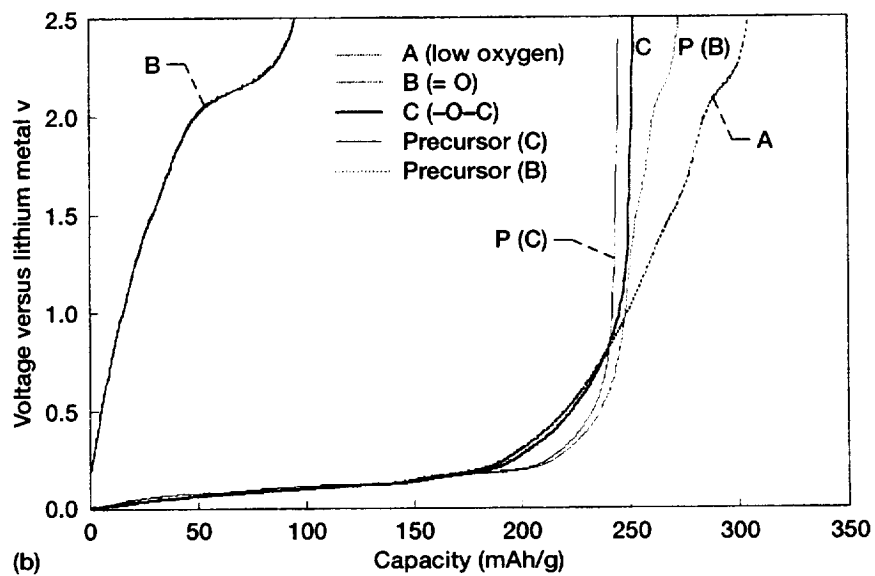
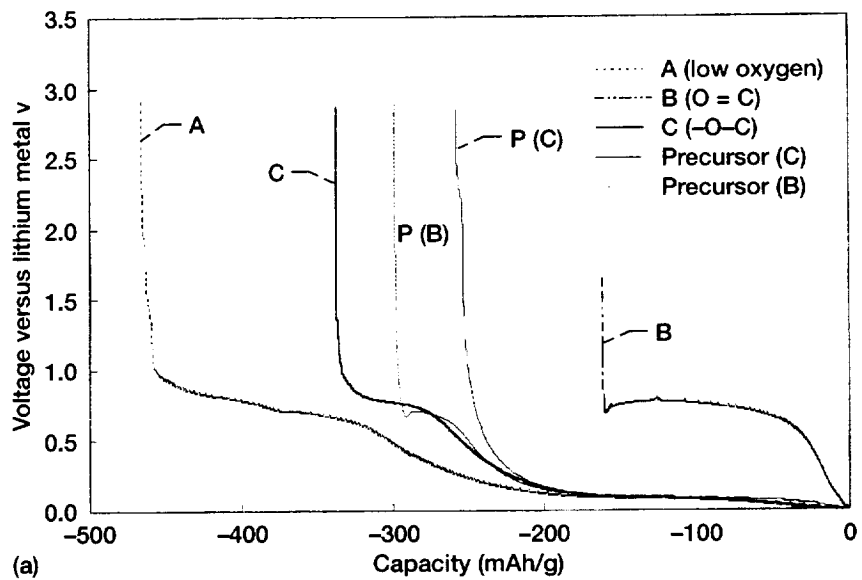


Figure 4.—Voltage of anodes made from carbon with different surfaces during first half cycles of lithium. (a) Insertion. (b) Release.

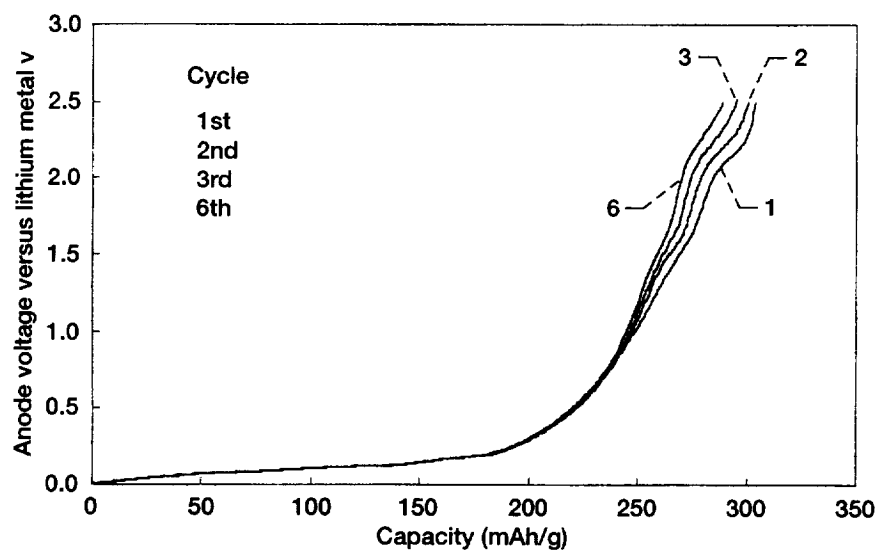


Figure 5.—Capacities of lithium release from an anode made from carbon containing active sites.

| REPORT DOCUMENTATION PAGE | | | Form Approved OMB No. 0704-0188 | |
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| 1. AGENCY USE ONLY (Leave blank) | | 2. REPORT DATE October 2001 | | 3. REPORT TYPE AND DATES COVERED Technical Memorandum |
| 4. TITLE AND SUBTITLE Effects of Surface Oxygen on the Performance of Carbon as an Anode in Lithium-Ion Batteries | | | 5. FUNDING NUMBERS WU-755-A4-13-00 | |
| 6. AUTHOR(S) Ching-cheh Hung and Gregory W. Clark | | | | |
| 7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) National Aeronautics and Space Administration John H. Glenn Research Center at Lewis Field Cleveland, Ohio 44135-3191 | | | 8. PERFORMING ORGANIZATION REPORT NUMBER E-12631 | |
| 9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) National Aeronautics and Space Administration Washington, DC 20546-0001 | | | 10. SPONSORING/MONITORING AGENCY REPORT NUMBER NASA TM-2001-210700 | |
| 11. SUPPLEMENTARY NOTES Prepared for the 198th Meeting sponsored by The Electrochemical Society, Inc., Phoenix, Arizona, October 22-27, 2000. Ching-cheh Hung, NASA Glenn Research Center; Gregory W. Clark, Department of Physics, Manchester College, North Manchester, Indiana 46962. Responsible person, Ching-cheh Hung, organization code 5480, 216-433-2302. | | | | |
| 12a. DISTRIBUTION/AVAILABILITY STATEMENT Unclassified - Unlimited Subject Categories: 23 and 25 Available electronically at http://gltrs.grc.nasa.gov/GLTRS This publication is available from the NASA Center for AeroSpace Information, 301-621-0390. | | | 12b. DISTRIBUTION CODE | |
| 13. ABSTRACT (Maximum 200 words) Carbon materials with similar bulk structure but different surface oxygen were compared for their performance as anodes in lithium-ion battery. The bulk structure was such that the graphene planes were perpendicular to the surface. Three types of surfaces were examined: surface containing C=O type oxygen, surface containing -O-C type oxygen, and surface containing high concentration of active sites. The test involved cycles of lithium insertion into and release from the carbon materials, which was in the half cells of carbon/saturated LiI-50/50 (vol %) EC and DMC/lithium. During the first cycle of lithium insertion the presence of adsorbed oxygen, -O-C type oxygen, active carbon sites, and C=O type oxygen resulted in the formation of solid-electrolyte interface (SEI) when the carbon's voltage relative to lithium metal was >1.35, 1 to 1.35, 0.5 to 1, and 0.67 to 0.7 V, respectively. An optimum -O-C type oxygen and a minimum C=O type oxygen was found to increase the reversible and decrease the irreversible capacity of carbon. Active sites on the carbon surface result in a large irreversible capacity and a second lithium insertion-release mechanism. However, this new mechanism has a short cycle life. | | | | |
| 14. SUBJECT TERMS Lithium-ion battery; Carbon anode; Surface oxygen; Active carbon sites; SEI formation | | | 15. NUMBER OF PAGES 19 | |
| | | | 16. PRICE CODE | |
| 17. SECURITY CLASSIFICATION OF REPORT Unclassified | 18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified | 19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified | 20. LIMITATION OF ABSTRACT | |

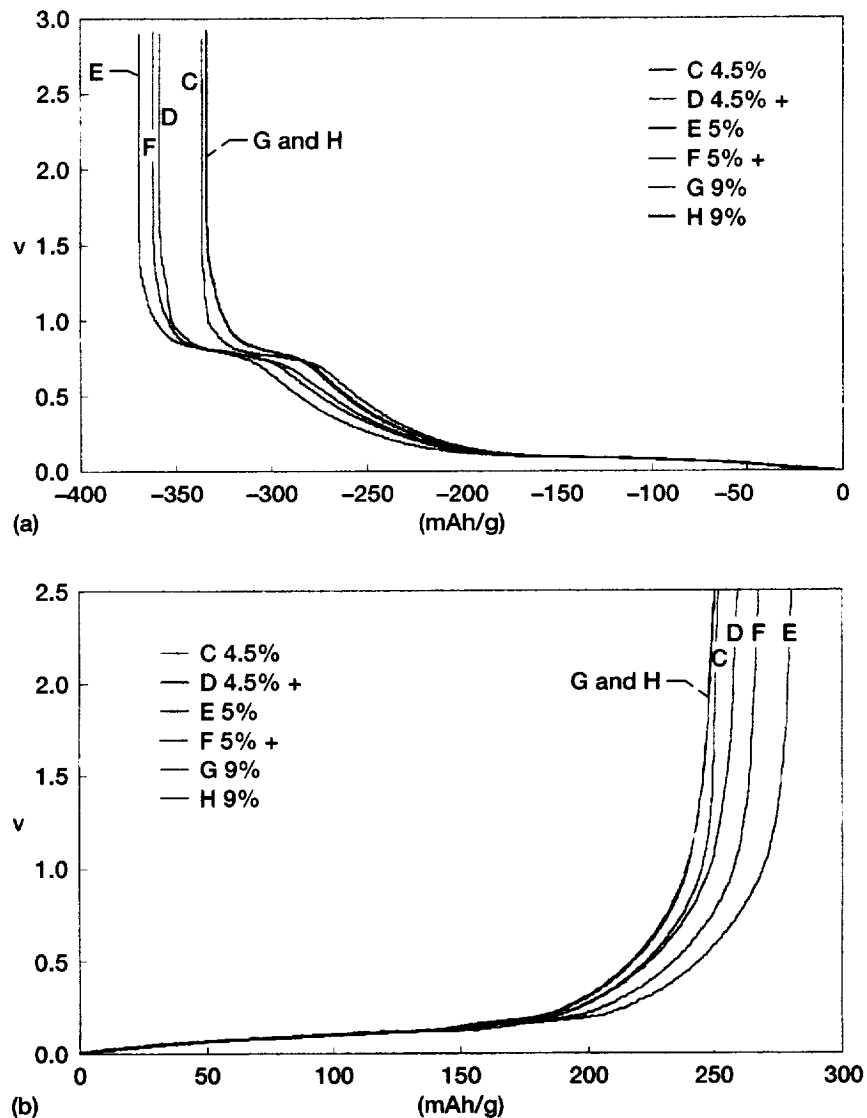


Figure 6.—Voltage of anodes made from carbon with different concentration of $-O-C$ type surface oxygen during the first half cycles of lithium. (a) Insertion. (b) Release.